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Simulation chamber studies on the NO_3 chemistry of atmospheric aldehydes

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[1] Absolute reaction rate studies of NO_3 radicals with 4 aldehydes were performed in the atmosphere simulation chamber SAPHIR at the Research Center Jülich. Rate coefficients (ethanal: 2.6 ± 0.5, propanal: 5.8 ± 1.0, butanal: 11.9 ± 1.4, benzaldehyde: 2.2 ± 0.6; in 10^{-15} cm^3 s^{-1} at 300 K) were determined from measured concentration–time profiles of aldehydes and NO_3 at near ambient conditions. The values for the aliphatic aldehydes are in good agreement with the most recent recommendations (IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry: Evaluated kinetic and photochemical data for atmospheric chemistry, 2005, available at http://www.iupac-kinetic.ch.cam.ac.uk). The measured concentration-time profiles of precursor aldehydes, NO_3, NO_2, and of product aldehydes were compared to model calculations based on the MCM v3 (Jenkin et al., 2003; Saunders et al., 2003). Differences between measurements and model are attributed to a major interference of the GC system to peroxyacyl nitrates. In addition modifications to the rate constants in the MCM are suggested. **Citation:** Bossmeyer, J., T. Brauers, C. Richter, F. Rohrer, R. Wegener, and A. Wahner (2006), Simulation chamber studies on the NO_3 chemistry of atmospheric aldehydes, *Geophys. Res. Lett.*, *33*, L18810, doi:10.1029/2006GL026778.

1. Introduction

[2] Aldehydes play an important role in the atmosphere as HO_x radical precursors. They originate from incomplete fossil fuel combustion and biomass burning. They are emitted by vegetation and produced during photochemical oxidation of volatile hydrocarbons [*Carlier et al.*, 1986]. Typically, the smaller the aldehyde the higher is its concentration in the atmosphere. In urban environments, mixing ratios of ethanal, propanal, butanal, and benzaldehyde can reach 18 ppb, 3 ppb, 1.4 ppb, and 1 ppb, respectively [*Finlayson-Pitts and Pitts*, 2000]. During daytime the fate of aldehydes is governed by photolysis and OH radical reactions while reactions with NO_3 radicals prevail during the night. On a global scale OH-reactions and photolysis dominate the loss of aldehydes. However, in mid-latitudinal winter, when diurnal averages of NO_3 and OH are around 10^9 cm^{-3} and 10^5 cm^{-3}, respectively, the impact of NO_3 may even exceed that of OH. Under these conditions, atmospheric residence times of aldehydes are on the order of several days.

[3] The rates of the NO_3 + aldehyde reactions were studied by different groups using absolute rate (AR) and relative rate (RR) techniques. The rates for the aliphatic aldehydes in all studies agree well within the stated error margins (see recommendation in the most recent IUPAC (IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry: Evaluated kinetic and photochemical data for atmospheric chemistry, 2005, available at http://www.iupac-kinetic.ch.cam.ac.uk) (hereinafter referred to as IUPAC website). For propanal, the most recent AR study supports this finding [*Cabañas et al.*, 2001]. However, their data for ethanal and butanal tend to be larger than the recommendation and other recent RR works [*D'Anna et al.*, 2001; *Papagni et al.*, 2000]. The AR study by *Ullerstam et al.* [2000] on butanal matches exactly the recommendation. So far, only two RR studies on the NO_3 + benzaldehyde reaction have been reported [*Atkinson et al.*, 1984; *Clifford et al.*, 2005], their results differ significantly. The temperature dependence of the rate coefficients has been studied [*Cabañas et al.*, 2001; *Ullerstam et al.*, 2000]. However, the temperature coefficients suffer from large uncertainties (IUPAC website).

[4] Like in the OH + aldehyde reaction, NO_3 abstracts a H-atom from the aldehyde group

$$RCHO + NO_3 + (O_2) \rightarrow RCO_3 + HNO_3 \quad (1)$$

producing an acyl peroxy radical [*D'Anna and Nielsen*, 1997]. The mechanism for the degradation of the aldehydes in this study is included in the Master Chemical Mechanism (MCM v3), which is a near-explicit reaction scheme of the gas phase degradation of VOCs and the resultant generation of ozone and other secondary pollutants [*Saunders et al.*, 2003; *Jenkin et al.*, 2003]. The reaction path taken from the MCM v3 for aliphatic aldehydes is outlined in Figure 1 which includes NO_3 (nighttime) reactions only, disregarding OH, NO, and photolysis. In the presence of NO_2 the formation and decay of peroxyacyl nitrates competes with the further reaction of the acyl peroxy radical with NO_3 or RO_2 yielding the next smaller aldehyde $R_{-1}CHO$.

[5] This work presents an absolute rate study of NO_3-reactions with 4 aldehydes under atmospheric conditions and a product analysis of the NO_3-degradation of propanal and butanal in comparison to model calculations based on the MCM v3.

2. Experimental

2.1. Instrumentation

[6] The atmosphere simulation chamber SAPHIR consists of a double-walled FEP bag of cylindrical shape (diameter 5 m, length 18 m, effective volume 270 m^3) operated with

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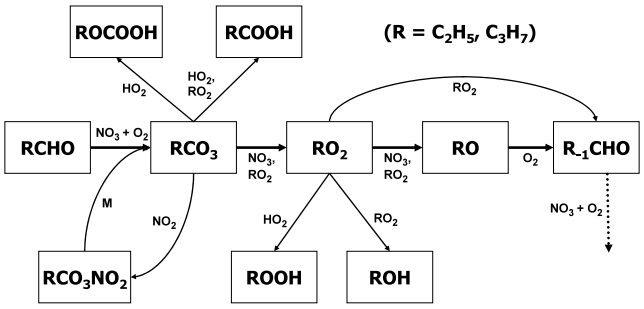

Figure 1. Degradation scheme of propanal and butanal as assumed by the MCM v3. Photolysis, NO- and OH-reactions not shown.

synthetic air (purity 99.9999%). A technical description of the chamber is given by *Rodríguez-Bares* [2003]. The chamber volume is kept at 40–60 Pa above ambient pressure to avoid contamination with outside air. The loss due to sampling extraction and wall leakage is replenished by synthetic air leading to a slow dilution of all species in the chamber, typically 2–3%/h. Shutters keep the chamber volume in darkness, but can be opened for daylight exposure. All experiments here were performed in darkness with photolysis frequencies at least a factor of 500 lower than outside. The chamber set-up comprises standard instruments for temperature, pressure, humidity, and gas replenishment flow. In addition, UV absorption (Ansyco O341M) is used to monitor O_3 while NO and NO_2 are measured by chemiluminescence (ECO Physics TR780).

[7] Aliphatic aldehydes are detected by a dual–column gas–chromatograph (GC) with cryo–focus module and two flame ionization detectors (Perkin–Elmer). Chamber air is sampled via a heated (330 K) inlet line. Before pre–concentration, H_2O is removed by a cold trap (223 K) and O_3 is depleted by NO (0.6 ppm). The sample is trapped on an adsorption tube filled with 36 mg Carbopack X and 18 mg Tenax TA at 243 K. After sampling, the tube is heated (523 K) and purged with Helium (99.9999%) desorbing onto a DB5 column. The first 13 min fraction, containing the aldehydes considered here, is directed to a Porabond Q column. The GC oven temperature is increased from 328 K to 493 K at 3 K/min. The system is calibrated on a certified standard (Apel–Riemer).

[8] NO_3 and benzaldehyde are measured by differential optical absorption spectroscopy (DOAS) with a multiple reflection set-up [*Bossmeyer*, 2006]. In short, light from a Xenon arc lamp (OSRAM, XBO 75W/2) is directed into a multi reflection cell of 20 m base length which is set up along the axis of the cylindrical SAPHIR chamber. After 48 travels the light is dispersed by a Czerny-Turner type spectrograph (Jobin Yvon, HR 460) equipped with 2 blazed holographic gratings. A PDA (Hamamatsu, S3904) detects the spectra on 1024 pixels covering a wavelength range of

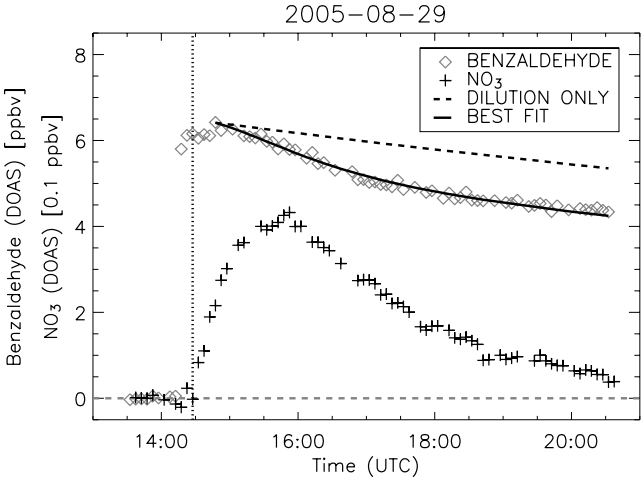

Figure 2. Measured concentration-time profiles of NO_3 and benzaldehyde compared to the best fit model and a dilution-only-scenario. The best fit was obtained by minimizing the χ^2 of the measured to the modeled aldehyde time profile with the rate coefficient as fit parameter. The vertical line indicates the start of the NO_3 production.

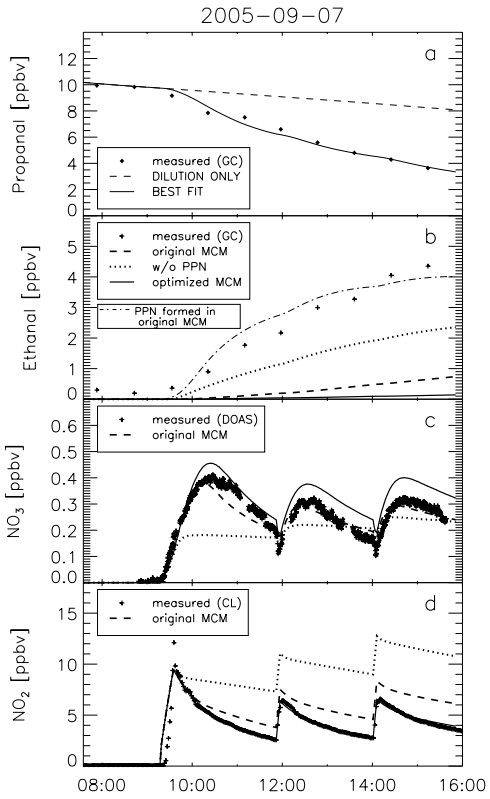

Figure 3. Measurements and model runs for the NO_3 + propanal experiment. (a) Determination of the absolute rate. (b, c, d) Dashed lines indicate model calculations with the original MCM mechanism, dotted lines without PPN production, and the full lines with increased stability of PPN. The dash-dotted line shows the modeled PPN which might cause an artifact in the GC measured ethanal. The fan did not operate during the first NO_2 injection resulting in a somewhat disturbed looking NO_2 measurement. However, the amount of NO_2 injected into the chamber is still correct since this difficulty only affects the NO_2 measurement close to the injection.

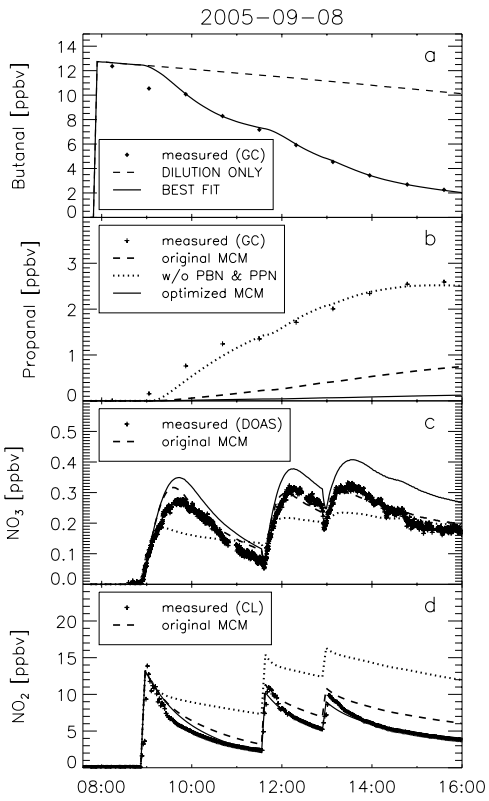

Figure 4. Time series in the NO_3 + butanal experiment. (a) Determination of the absolute rate. (b, c, d) Comparison of measured propanal, NO_3, and NO_2 with 3 different model runs (for explanation see text).

44 nm or 88 nm depending on the selected grating. Spectra are acquired through a controller (Hoffmann Messtechnik) connected to a PC.

[9] NO_3 radicals were measured by DOAS at a spectral resolution of 0.4 nm in the range from 617–670 nm using the absorption cross section of *Sander* [1986]. In the Aug 29 experiment, benzaldehyde was also measured by DOAS (resolution: 0.2 nm; region: 273–286 nm; cross section [*Etzkorn et al.*, 1999]). The two wavelength regions were alternated every 5 min. In all other experiments NO_3 data were recorded continuously at 30 s time steps.

2.2. Experiment Description

[10] All experiments were performed in a similar manner:

[11] (1) Before each experiment the chamber was flushed with clean, dry synthetic air to remove the remains from previous experiments.

[12] (2) The selected aldehyde was added by injection of a high purity (propanal >98%; else >99%) liquid (8–13 μl). Mixing ratios calculated from the injected amounts agreed with the GC measurements directly after injection.

[13] (3) 250–500 ppm CO were added to suppress the effect of OH radicals arising from secondary reactions (except benzaldehyde experiment, where OH is not formed).

[14] (4) 100–150 ppb O_3 was added, generated in an external silent discharge ozonizer.

[15] (5) 10 ppb NO_2 were injected from a mixture of 500 ppm NO_2 in N_2. This starts the production of NO_3 through the NO_2 + O_3 reaction. Additional quantities of NO_2 were injected during the experiments with the aliphatic aldehydes to fuel NO_3 production and thus enlarge conversion rates.

[16] During injections a powerful fan was operated for one minute to ensure rapid mixing inside the chamber. After the first injection of NO_2, the experiments proceeded for about 6 hours.

3. Results and Discussion

3.1. Kinetics of the NO_3 + Aldehyde Reactions

[17] During 4 chamber experiments we simultaneously recorded the concentrations of the respective aldehyde and of NO_3 (Figures 2, 3a, and 4a). The aldehyde concentration [RCHO] in the chamber (R = CH_3, C_2H_5, C_3H_7, C_6H_5) depends on the dilution and the NO_3-reaction only, since OH-reactions were suppressed by excess CO when required. Hence, the decay of the aldehyde is described by

$$d[\mathrm{RCHO}]/dt = -(k_{\mathrm{dil}} + k_{\mathrm{NO_3}}[\mathrm{NO_3}]) \times [\mathrm{RCHO}] \qquad (2)$$

where k_{dil} represents the dilution rate, calculated from the replenishment flow and the chamber volume. We constrained the fit with the measured k_{dil} and [NO_3] averaged to a common 5-min time interval. The initial [RCHO] was taken from the measured aldehyde data point, when the injection was homogeneously distributed in the chamber.

[18] In order to determine $k_{\mathrm{NO_3}}$ we performed a weighted least squares fit of the modeled to the measured aldehyde data. We also included the temperature dependence for ethanal and butanal described in the current IUPAC (website, 2005) recommendation. The decay of the aldehyde is closely described by the fitted curve (Figures 2, 3a, and 4a). For comparison, we included the curve calculated for dilution-only, demonstrating the significant effect of the NO_3. Uncertainties of the rate constants were deduced from the accuracies of the measured data (benzaldehyde (DOAS): 5%, aliphatic aldehydes (GC): 8%, NO_3 (DOAS): 8%, dilution: 3%).

[19] For the aliphatic aldehydes, our rate coefficients support the recommendations (IUPAC website) (Table 1). For benzaldehyde two contradicting determinations were

Table 1. Rate Coefficients of NO_3 + Aldehyde Reactions[a]

Aldehyde	T, K	k, 10^{-15} cm^3 s^{-1}	Reference
CH_3CHO	300 ± 3	2.6 ± 0.5 (1-σ)	This work
	298	$2.7^{+1.6}_{-1.0}$ (2-σ)	(IUPAC website)
C_2H_5CHO	300 ± 3	5.8 ± 1.0 (1-σ)	This work
	298	$6.5^{+3.8}_{-2.3}$ (2-σ)	(IUPAC website)
C_3H_7CHO	301 ± 2	11.9 ± 1.4 (1-σ)	This work
	298	$11.0^{+4.5}_{-3.2}$ (2-σ)	(IUPAC website)
C_6H_5CHO	301 ± 3	2.2 ± 0.6 (1-σ)	This work
	294	2.6 ± 0.1 (1-σ)	[*Atkinson*, 1991]
	295 ± 2	4.3 ± 0.3 (1-σ)	[*Clifford et al.*, 2005]

[a]Confidence limits of uncertainties: IUPAC website (2005) 95%, this work 68%. For benzaldehyde no recommendation is available, instead the two RR studies are quoted, their errors denote 1-σ.

published. Within the stated errors, our data are in good agreement with *Atkinson* [1991]. The value of *Clifford et al.* [2005], however, exceeds ours significantly.

3.2. Products of the Reactions NO_3 + Propanal and NO_3 + Butanal

[20] In the NO_3 + aldehyde reactions the formation of smaller aldehydes is expected when the acyl peroxy radical further reacts with NO_3 or RO_2 (Figure 1). In the case of the propanal and butanal experiments our GC detected the product aldehydes (ethanal; ethanal + propanal) simultaneously with the reactant aldehyde (Figures 3b and 4b). The results from both experiments were compared to mixing ratios calculated using the MCM modules for propanal and butanal. The rate coefficients of the NO_3 + aldehyde reactions were updated from the kinetic study. The model was constrained to 5-min averaged measured data of temperature, pressure, and replenishment flow. NO_2, NO_3, O_3, and the aldehydes were calculated taking into account the appropriate injection times and quantities as time dependent sources for these species.

[21] In the propanal experiment the measured ethanal mixing ratio reaches 4 ppb at the end of the experiment when 5 ppb of propanal had reacted with NO_3 (Figure 3b). However, the ethanal reaches only 0.6 ppb in the MCM model where the reaction proceeds via production of peroxypropionyl nitrate (PPN; see dash-dotted line in Figure 3b). Since the amount of NO_2 stored in PPN is quite large, the measured NO_2 concentrations (Figure 3d) indicate that the GC determination of 4 ppb ethanal is implausible. If NO_2 is not accumulated in the form of PPN its concentration is calculated (dotted line in Figure 3d) approximately 6 ppb (200%) higher than the measurements at the end of the experiment. The dashed lines indicate model calculations for PPN and NO_2 using the original MCM. Since measured NO_2 points to a somewhat larger quantity of NO_2 stored in PPN we tried to increase the rate constants for the production of PPN and to decrease its thermal decomposition, both by a factor of four. The result for NO_2 (full line, Figure 3d) is quite convincing. However, the calculated NO_3 concentrations are 20% higher than the measured values which have a 7% accuracy. These findings indicate that the chemistry related to this chemical system is not fully covered by the current MCM.

[22] The experiment with butanal gave similar results (Figure 4). Approximately 10 ppb of butanal reacted with NO_3 resulting in 2.5 ppb of propanal and 2.5 ppb of ethanal in the GC measurements whereas the MCM calculates 0.8 ppb propanal and negligible amounts of ethanal. Again, the NO_2 measurements in Figure 4d suggest the fixation of more than 10 ppb of NO_X in the form of NO_3, N_2O_5, PBN (presumably the dominating reservoir), and PPN. Optimizing the MCM model by increasing the rate constants for the production of PBN and PPN and by decreasing their thermal decompositions all by a factor of four results in a quite satisfying agreement between NO_2 measurement and model calculation.

[23] Both, the reactions of propanal and of butanal with NO_3 showed significant amounts of the next smaller aldehydes in the GC measurements. The analysis of the NO_X budget disagrees with a fast production of these product aldehydes. We therefore reason that the peroxyacyl nitrates PPN and PBN when sampled and heated in the pre–concentration system of the GC are almost quantitatively converted to smaller aldehydes. The thermal decomposition products of PPN and PBN could react most probably with NO which is added for O_3 destruction.

4. Conclusions

[24] Our rate coefficients for the NO_3-reactions with aliphatic aldehydes are in good agreement with the literature. Moreover, we present the first absolute rate study on the NO_3+ benzaldehyde reaction, which contradicts a recent relative rate work.

[25] Like in the MCM model, the reactions are shown to proceed via the production of peroxyacyl nitrates by analysis of the NO_X budget. The analysis suggests a somewhat larger stability of PPN and PBN compared to the MCM model where they are treated like the smaller homologous molecule PAN (peroxyacetyl nitrate). The observation of product aldehydes by GC analysis points to a major interference to precursor peroxyacyl nitrates probably caused by follow-up reactions inside its pre–concentration system. This interference would also affect GC measurements during field experiments pretending aldehyde concentrations instead of peroxyacyl nitrates. In order to clarify these open questions further chamber experiments with simultaneous measurements of all NO_Y components are required.

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